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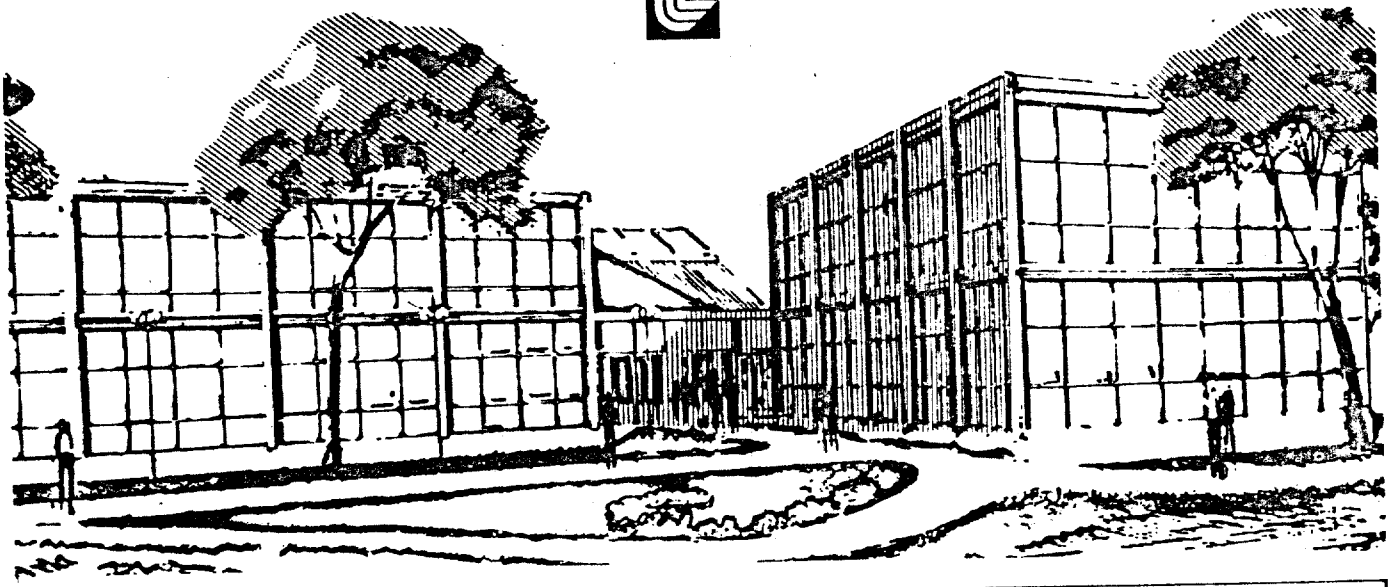

DEUTERIUM SEPARATION BY CO_2 LASER DISSOCIATION OF FLUOROMETHANES[†]

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ABSTRACT

Difluoromethane and trifluoromethane are the best candidate molecules for large-scale laser separation of deuterium. Absorption selectivity exceeds 1000 for both molecules. Dissociation with 2 nanosecond pulses permits high dissociation yield to 0.5 atmosphere with deuterium enrichment factors of 2000 for difluoromethane and 10,000 for trifluoromethane.

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SUMMARY

An extensive evaluation of candidate molecular systems suitable for large-scale laser separation of deuterium has resulted in the selection of only two near-optimum molecules--difluoromethane and trifluoromethane. Both molecules undergo deuterium-separation multiple-photon dissociation (MPD) following excitation by a CO_2 laser near 10.2-10.5 micron. Both satisfy the fundamental requirements for large-scale process viability, namely, greater than 1000-1 deuterium optical selectivity (σ_D/σ_H) in multiple-photon absorption, high dissociation yield near atmospheric pressure, and greater than 1000-fold single-step deuterium enrichment, β, in the dissociation products.

This paper presents the results of experiments in which β is measured in CHF_3 by carbon-isotope labelling of the reactants along with recent measurements of β and σ_D/σ_H in both molecules at high pressures (> 0.1 atm) using a short pulse CO_2 laser (FWHM $\simeq$ 2 nsec).

It is difficult to measure the DF photoproduct of CDF_3 MPD (10.3μ) directly in laboratory experiments due to the reactivity of DF with the walls of the reaction cell. However, the D/H ratio in the product (and therefore β) may be determined directly by irradiating a mixture of $^{12}CDF_3/^{13}CHF_3$ and then measuring the $^{12}C/^{13}C$ ratio in the C_2F_4 product. Tetrafluoroethene is formed by recombination of CF_2 radicals which are produced in the nascent MPD step along with DF. In a pure $^{12}CDF_3/^{13}CHF_3$ mixture there is a one-to-one correspondence between the formation of a

DF(HF) and the appearance of a $^{12}C(^{13}C)$ in the C_2F_4 product; this is actually only approximately true in this experiment since because of the isotopic purity of the starting material is only 85% ^{13}C [$^{13}CHF_3$], but is easily taken into account. β was measured this way at a variety of wavelengths and other operating conditions using mixtures of 20 torr argon plus $\sim$ 0.2 torr $^{13}CHF_3$, which was doped with about a 10^{-3} impurity of $^{12}CDF_3$. At 30 J/cm^2 fluence the CDF_3 dissociation probability is known to be nearly unity.(1) At this fluence β was found to be 2500 at 10.15μ, and increased rapidly toward longer wavelengths and was > 20,000 from 10.25-10.35μ. In addition, at 10.3μ, β was observed to decrease at higher fluences.

Very high (>> 1000) values of the deuterium enrichment factor and absorption optical selectivity at > 0.1 atm pressure are necessary for industrially viable deuterium separation. In order to avoid collisional quenching of photoproduct yield, the sample must be irradiated by a short pulse CO_2 laser (FWHM $\sim$ 2 nsec). The results of preliminary measurements of these quantities (performed at the Los Alamos Scientific Laboratory in collaboration with S. J. Thomas of LASL) have been previously reported(2) by the authors. The results based on more refined analysis of this data are now presented for CDF_3 (R(26), 10.2μ) $\beta = 11{,}500\ ^{+6500}_{-2500}$ at 100 torr for 30 J/cm^2 and σ_D/σ_H = 1800 at 2 J/cm^2 fluence, and $CHDF_2$(P(14),10.5μ): $\beta = 2500 \pm 200$ at 200 torr for 23 J/cm^2 and σ_D/σ_H = 500 at 2 J/cm^2 fluence.

Only by using $\sim$ 2 nanosecond duration CO_2 laser pulses could high pressure operation be achieved. The photodissociation yield was near unity at 30 J/cm^2 for trifluoromethane and was found to be fairly independent of pressure up to 400 torr, beyond which yield fell slowly. Difluoromethane yield saturated near 29 J/cm^2 out to 400 torr, limited by breakdown within the gas. Additional results will be presented, along with their implication for photochemical production of heavy water.

REFERENCES

(1) I. P. Herman and J. B. Marling, Chem. Phys. Lett. 64, 75 (1979).

(2) J. B. Marling, I. P. Herman and S. J. Thomas, 1979 IEEE/OSA Conference on Laser Engineering and Applications, Presentation #4.2.